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(71) Applicant(s)  
**Domino Printing Sciences Plc**  
  
**(Incorporated in the United Kingdom)**  
  
**Bar Hill, CAMBRIDGE, CB3 8TU, United Kingdom**

(72) Inventor(s)  
**Raymond David Burr**  
**Naser Reza**  
**Alan Lionel Hudd**  
**Shaun Christopher Hazlewood**  
**Jenny Marie Bowles**

(74) Agent and/or Address for Service  
**Kilburn & Strode**  
**30 John Street, LONDON, WC1N 2DD,**  
**United Kingdom**

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**C3V VAE**  
**C3W W308**  
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(56) Documents Cited  
**GB 2238792 A**      **EP 0359129 A**      **EP 0328301 A**  
**US 4895888 A**      **US 4820765 A**      **US 4690712 A**

(58) Field of Search  
**UK CL (Edition M ) C3V VAE VCA**  
**INT CL<sup>5</sup> C09D 11/10**  
**ONLINE DATABASES:EDOC,WPI,WPIL,CLAIMS**

(54) **INKS**

(57) Inks for continuous ink jet printers are disclosed containing polyamide resins as binders characterised by their Glass Transition Temperature values.

**GB 2 286 402 A**

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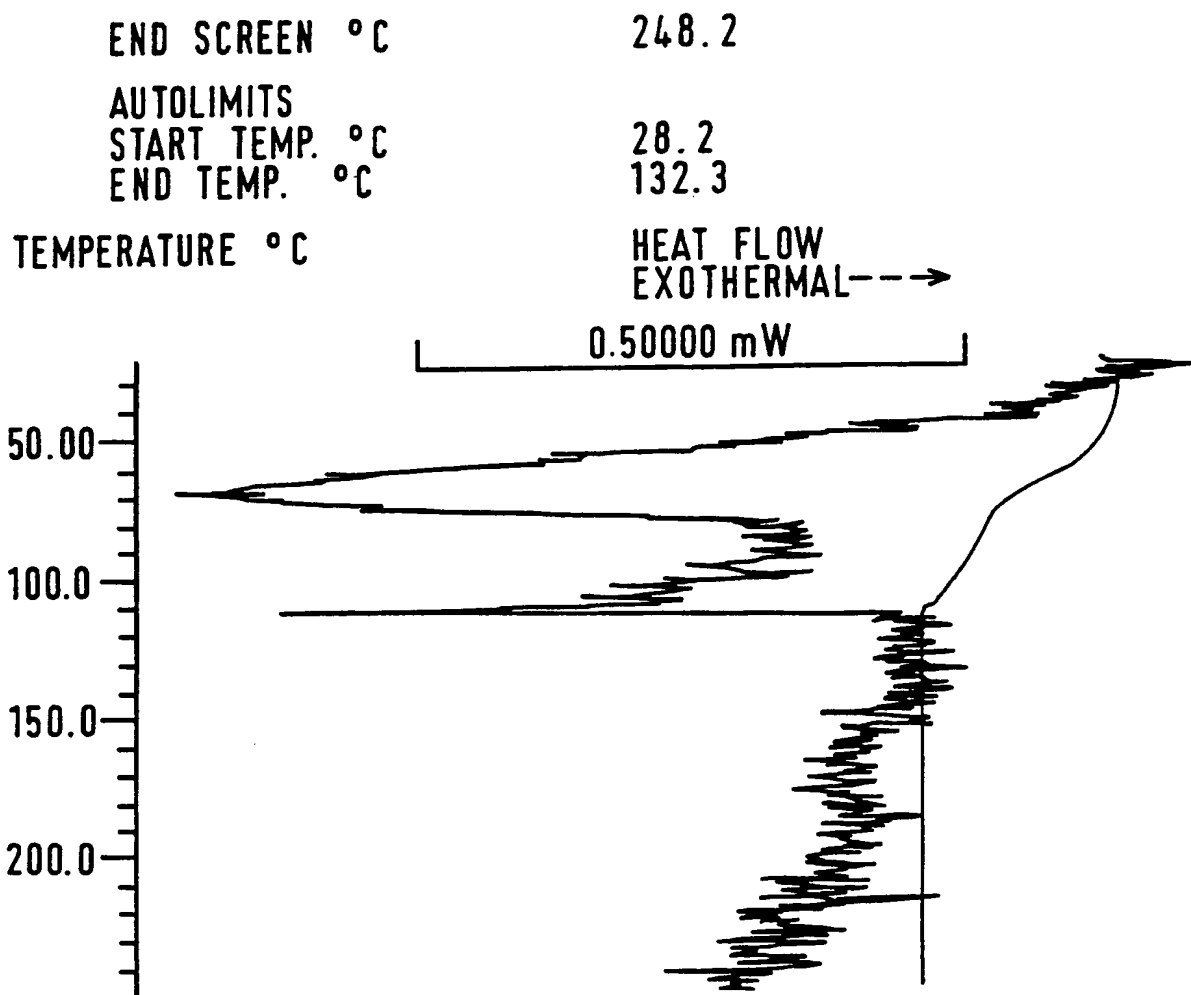


FIG. 1A1.

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GLASS TRANSITION

AUTOLIMIT 0/1

START TEMP. °C

END TEMP. °C

BASELINE TYPE

PLOT CM

PLOT MODE

IDENT. NO.

RATE K/MIN.

WEIGHT mg

1

-40

160

1

10

101

6

5

6.91

TEMPERATURE °C

HEAT FLOW  
EXOTHERMAL --->

0.50000 mW

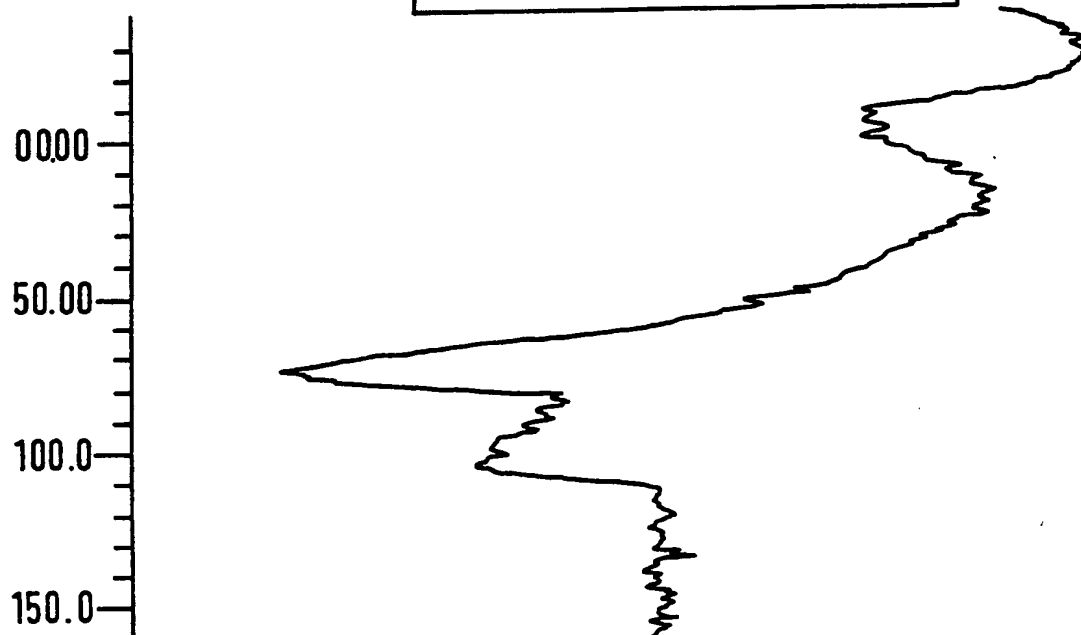
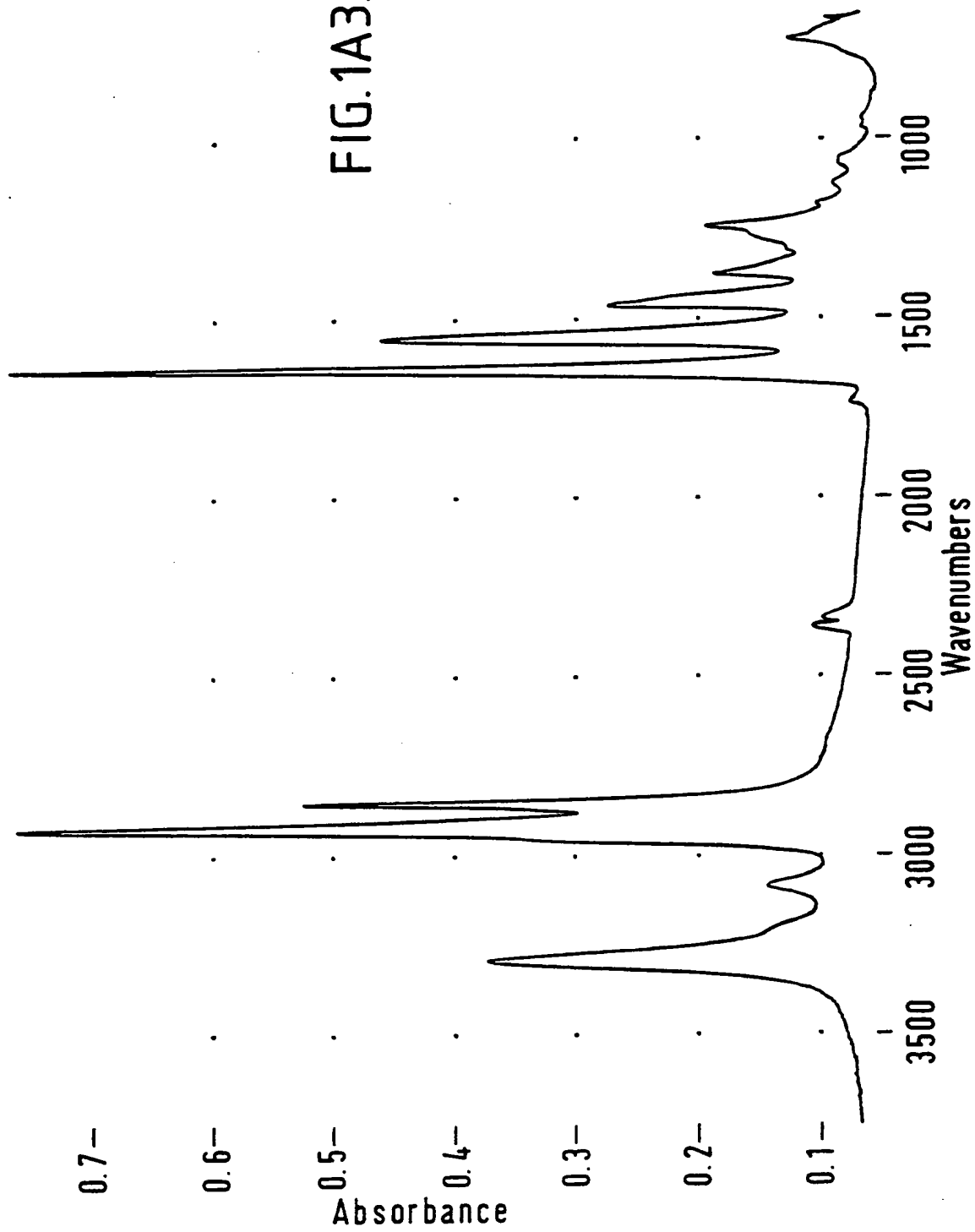


FIG. 1A2.

FIG. 1A3.



SPECIMEN F, CODE 1452 in C0300 for 1H

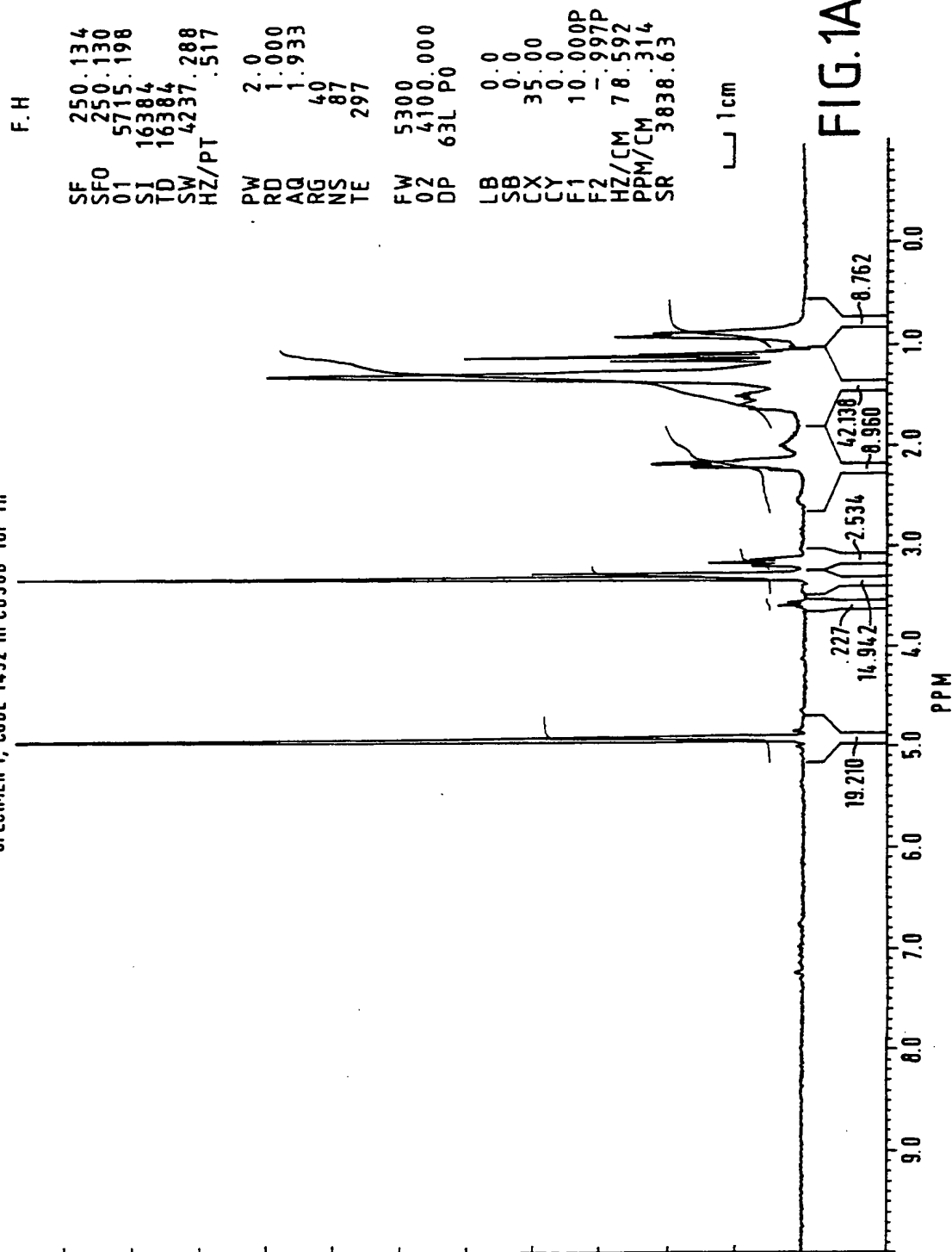
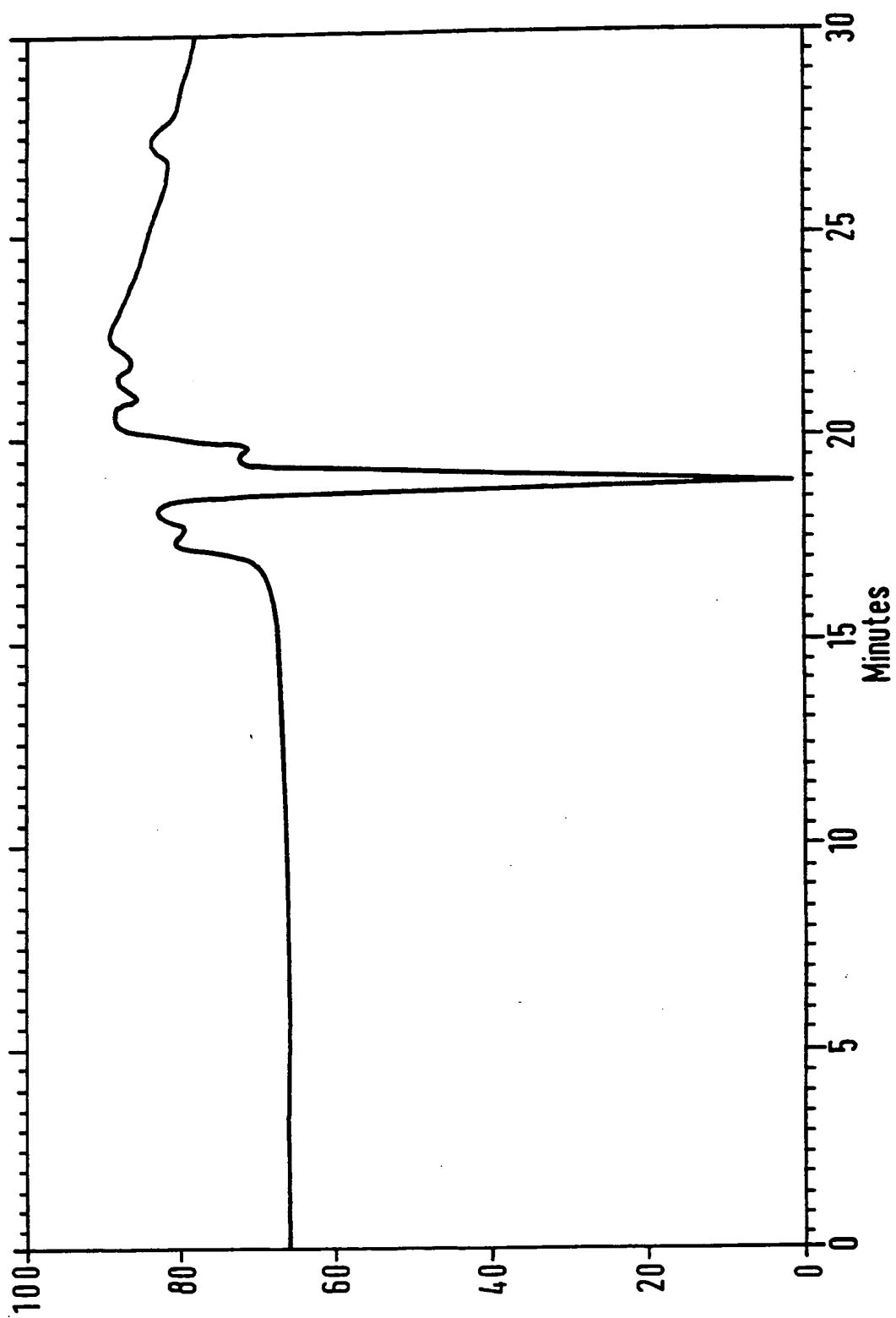
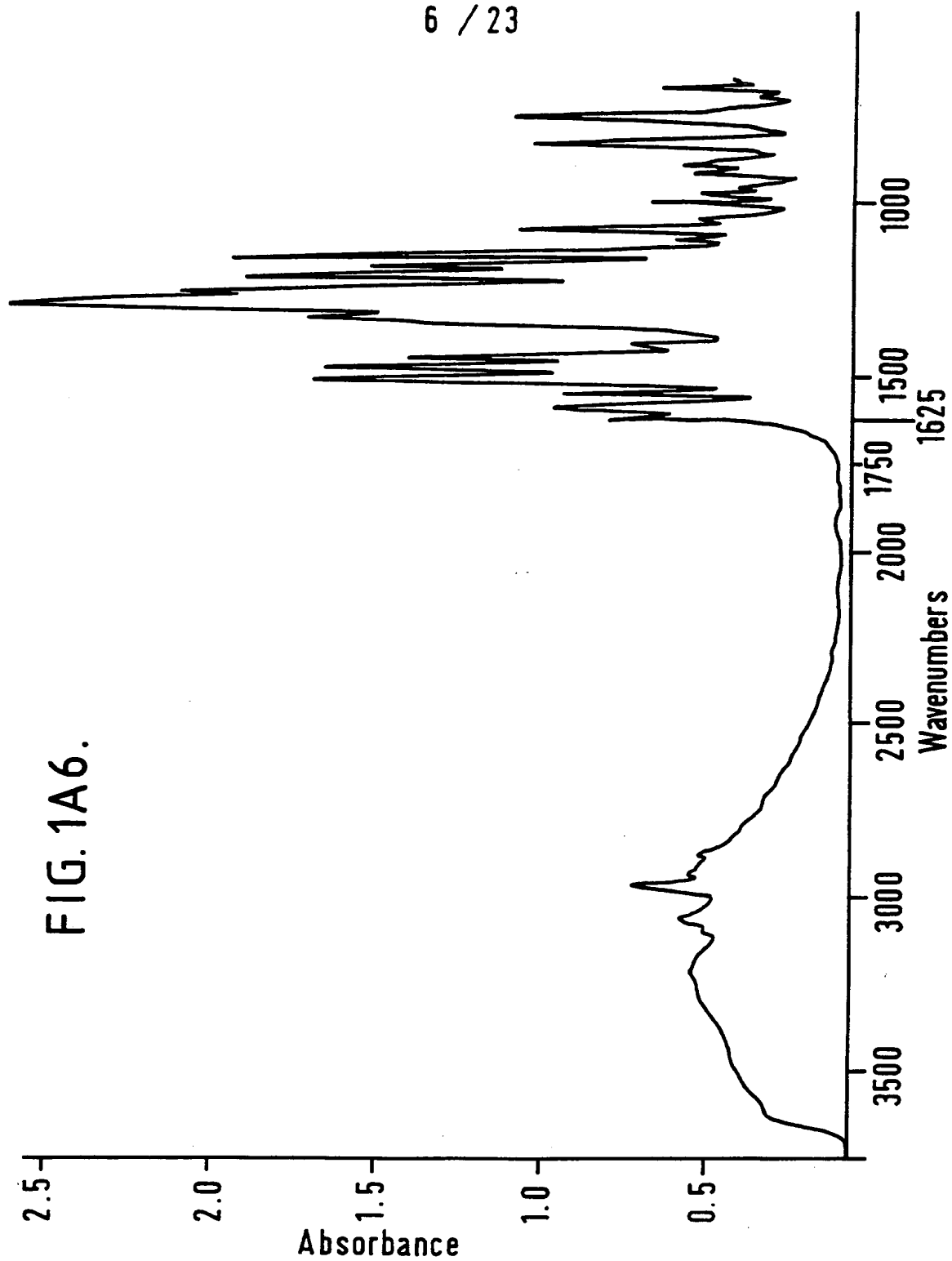


FIG. 1A4.

FIG. 1A5.





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GLASS TRANSITION

AUTOLIMIT 0/1

START TEMP. °C

END TEMP. °C

BASELINE TYPE

PLOT CM

PLOT MODE

IDENT. NO.

RATE K/MIN.

WEIGHT mg

1

-40

200

1

10

101

7

5

7.04

TEMPERATURE °C

HEAT FLOW

EXOTHERMAL -->

0.50000 mW

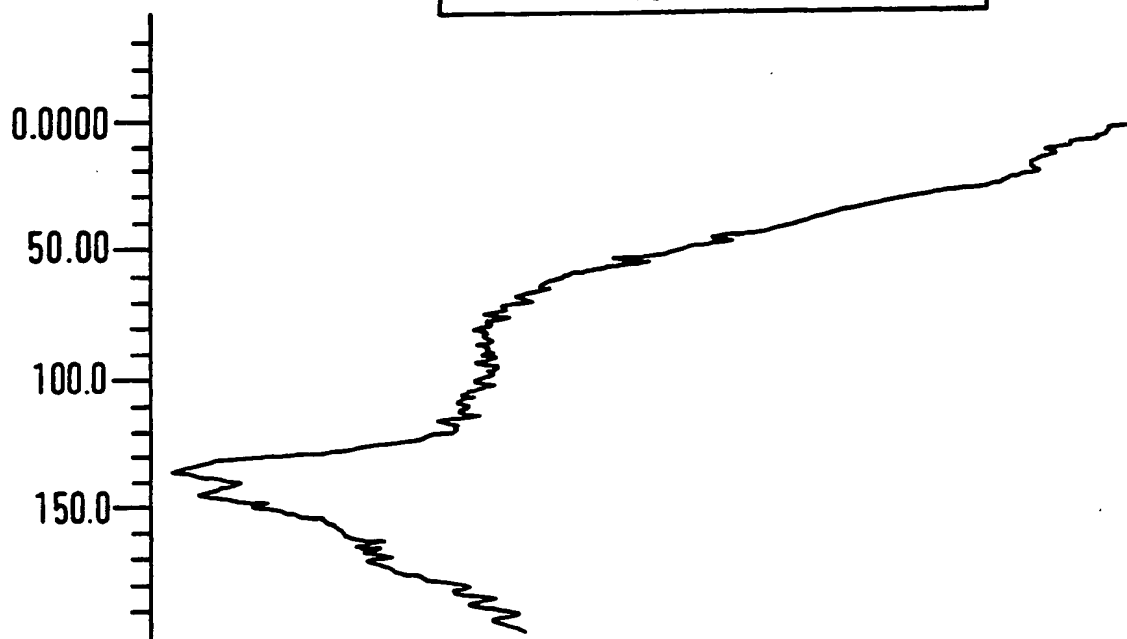


FIG. 1B1.



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FIG.1B3.

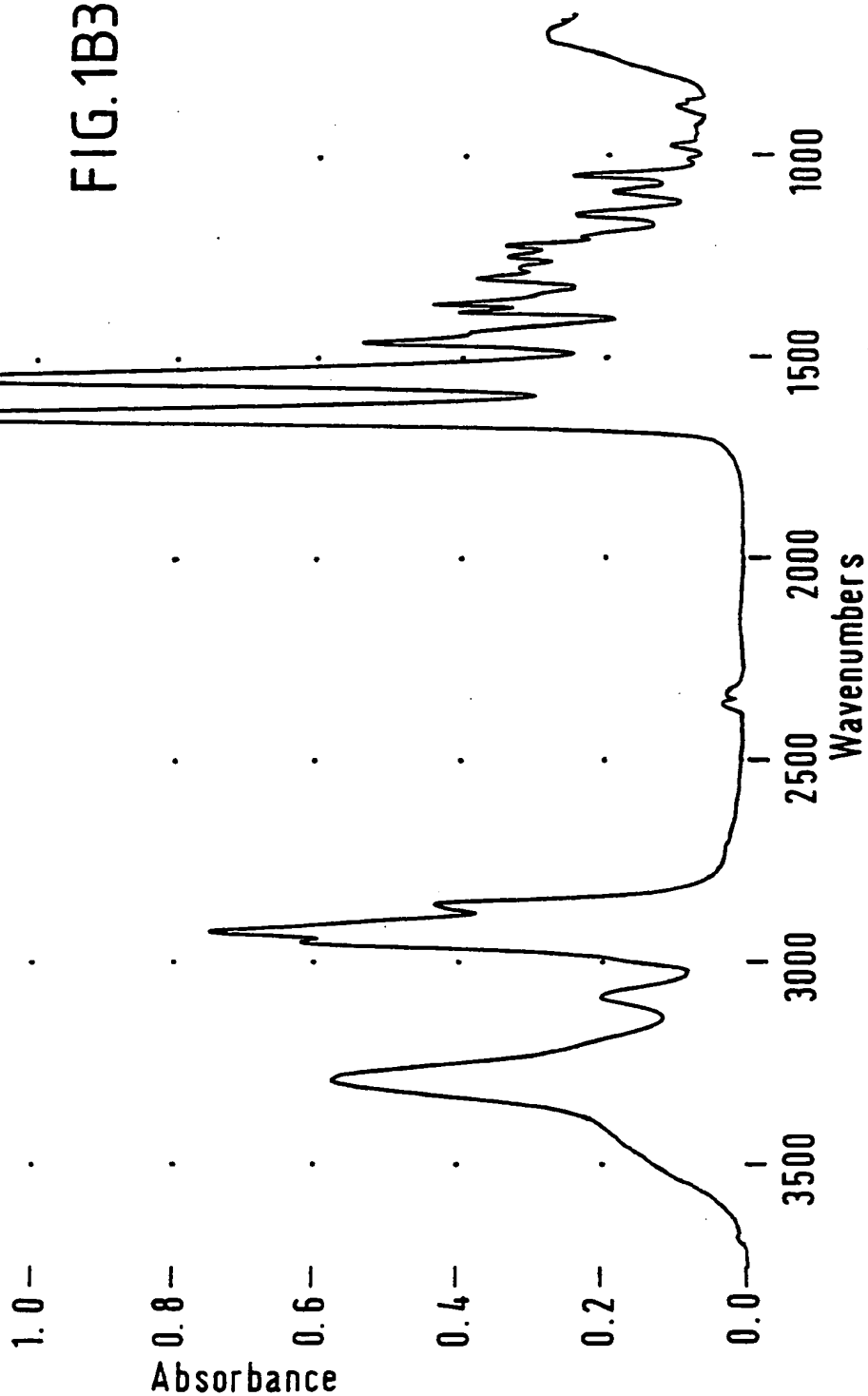


FIG.1B4.

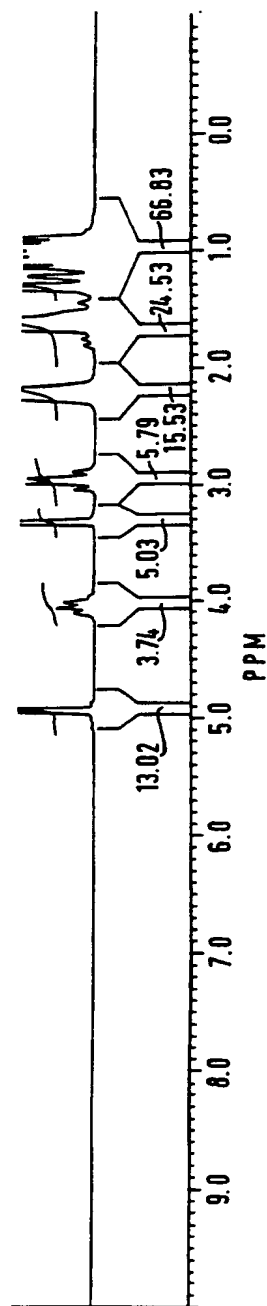


FIG.1B5.

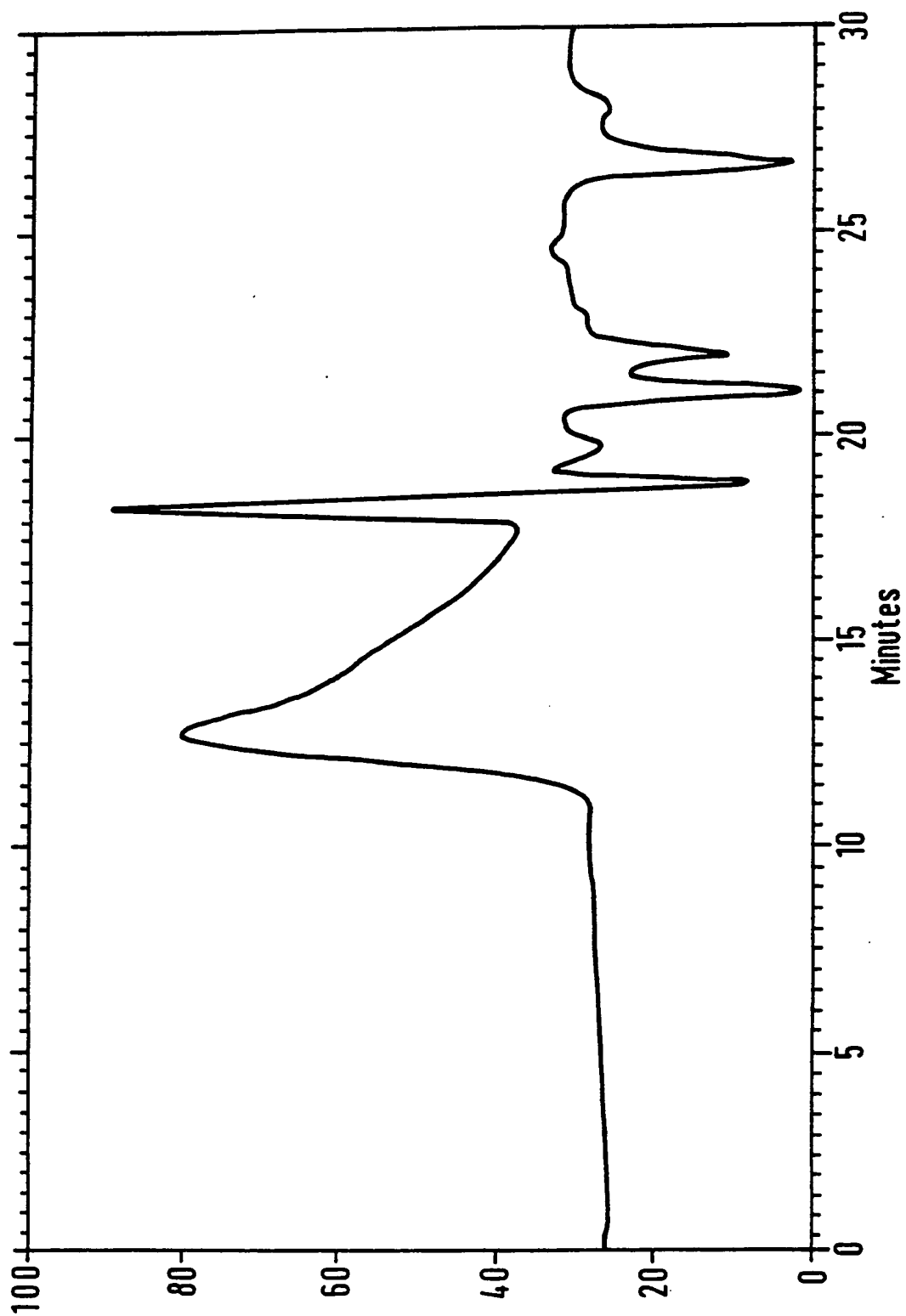
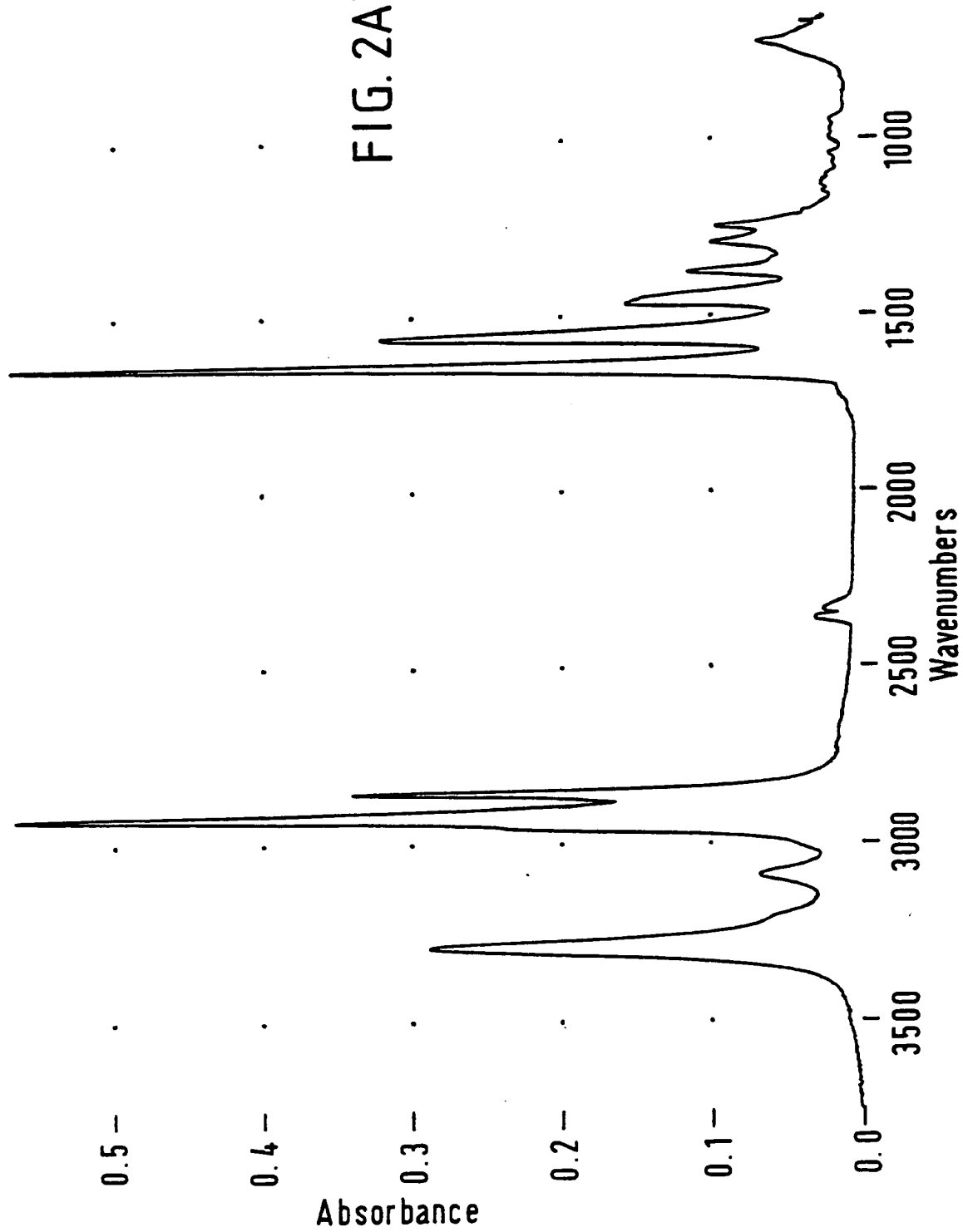


FIG. 2A3.



EURELON 966, CODE 1450 in CD300 for 1H

EUR966.H

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SF	250.134
SFO	250.130
O1	5715.198
SI	16384
TD	16384
SW	4237.288
HZ/PT	.517
PW	2.0
RD	1.000
AQ	1.933
RG	16
NS	96
TE	297
FW	5300
O2	4100.000
DP	63L P0
LB	0.0
GB	0.0
CX	35.00
CY	0.0
F1	10.000P
F2	-.997P
HZ/CM	78.592
PPM/CM	.314
SR	3838.63

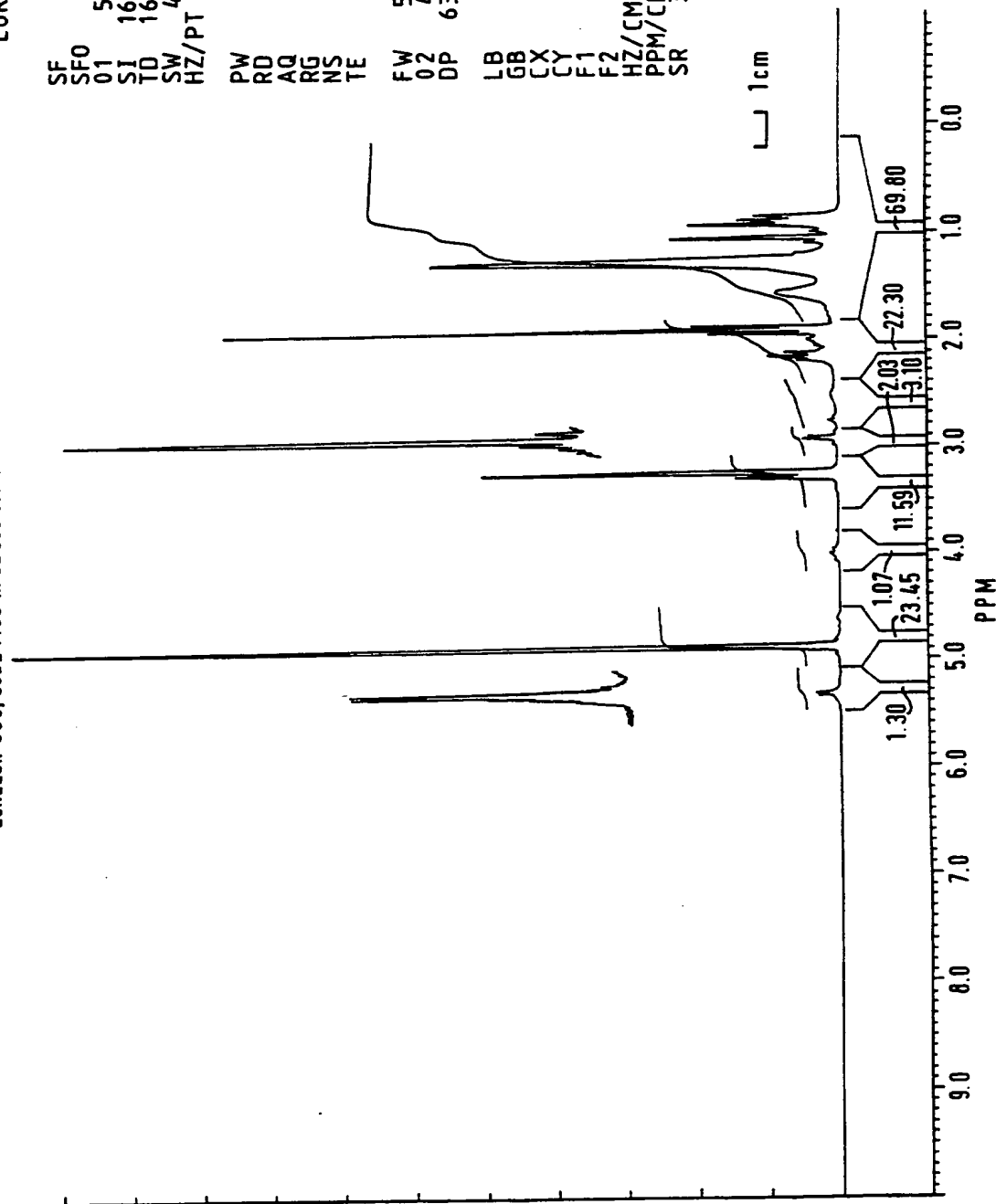
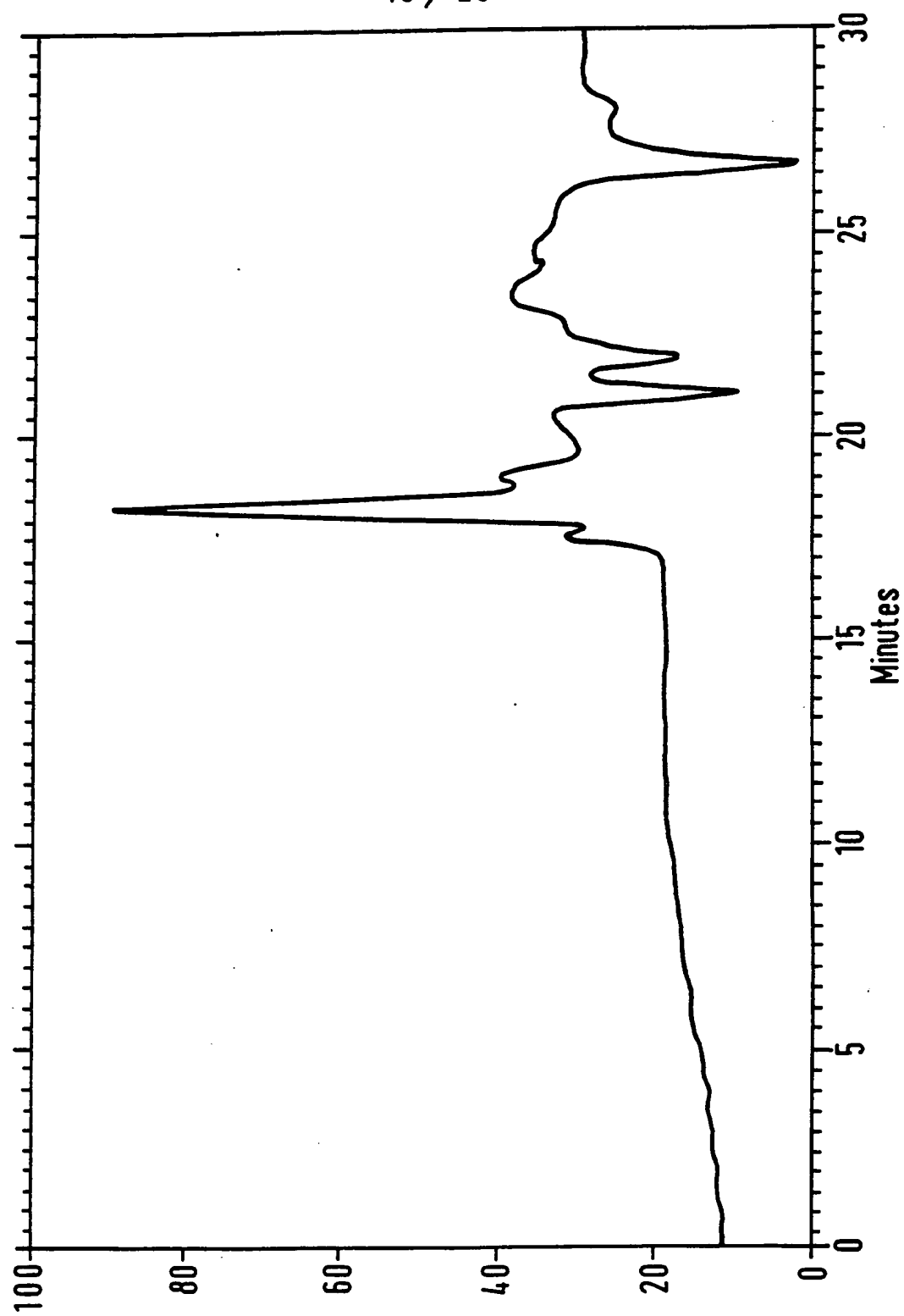


FIG. 2A4

FIG. 2A5.



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GLASS TRANSITION

AUTOLIMIT 0/1

START TEMP. °C

END TEMP. °C

BASELINE TYPE

PLOT CM

PLOT MODE

IDENT. NO.

RATE K/MIN.

WEIGHT mG

END SCREEN °C

WARNING

1

10

200

1

10

101

132

5

8.60

198.2

6

TEMPERATURE °C

HEAT FLOW

EXOTHERMAL --->

0.50000 mW

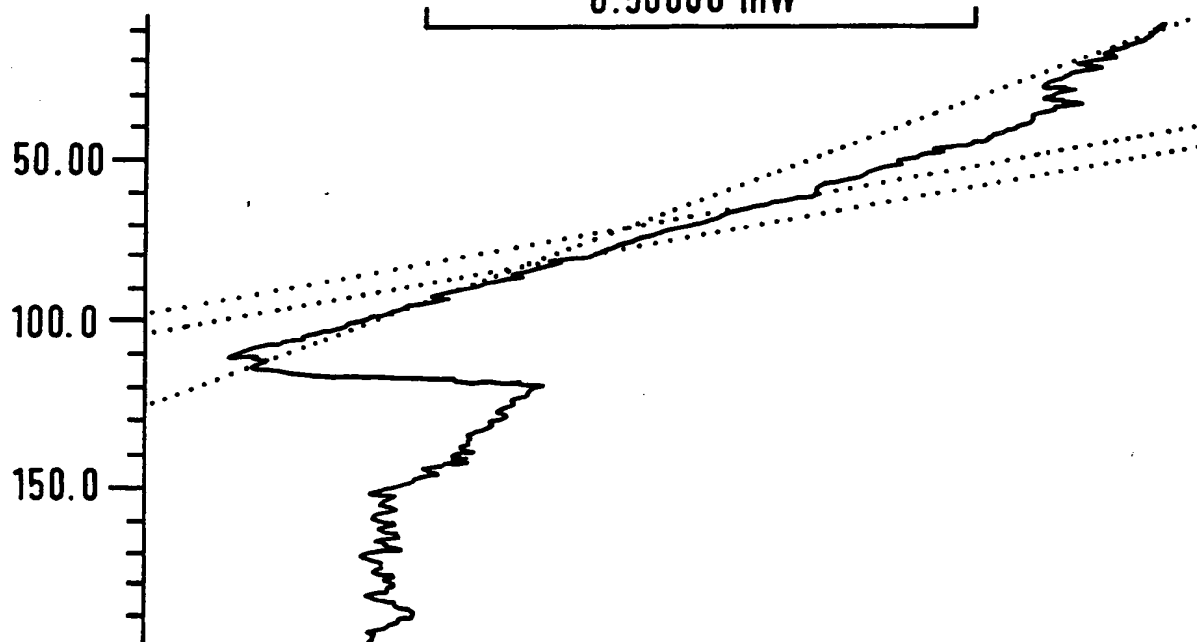
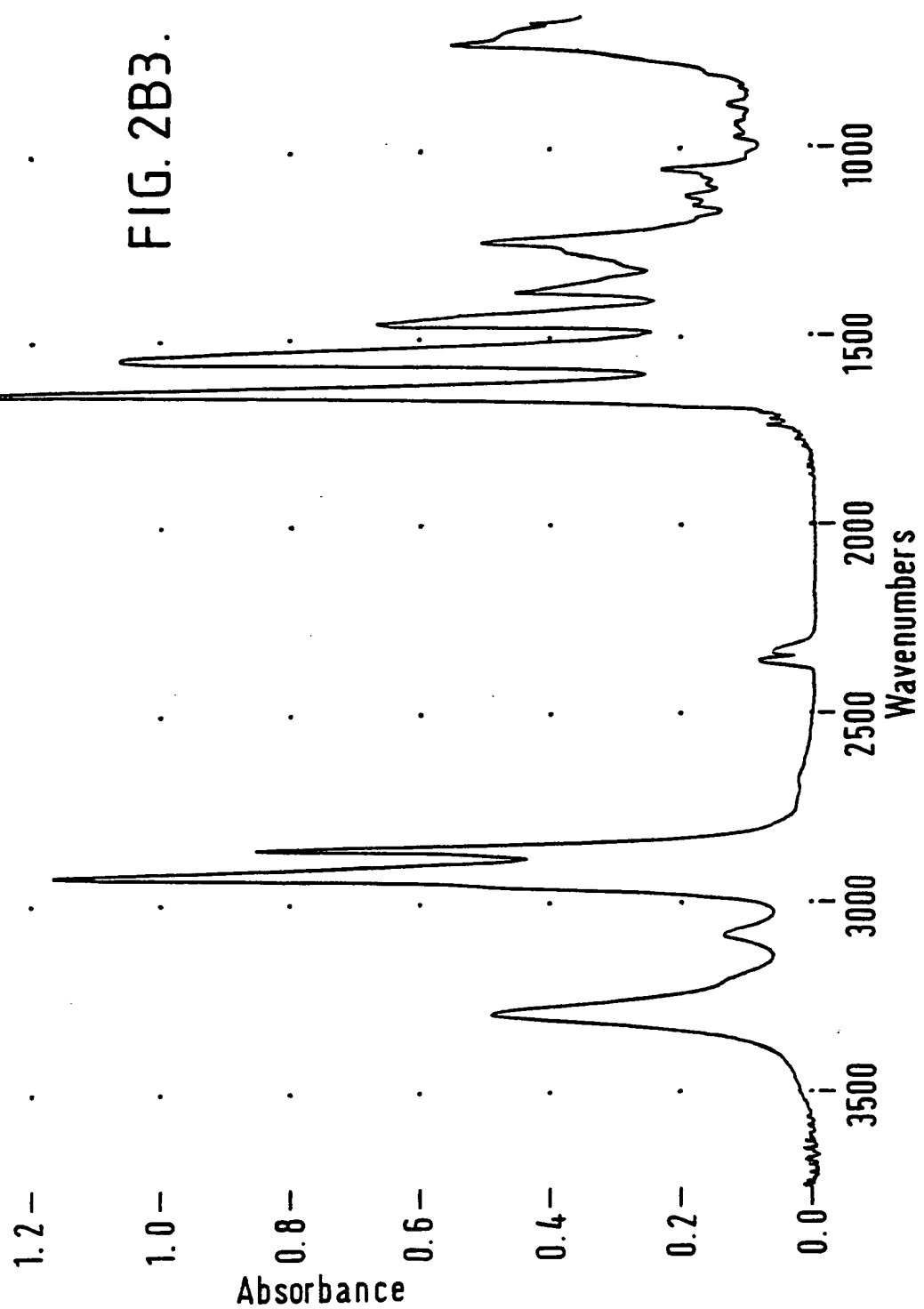
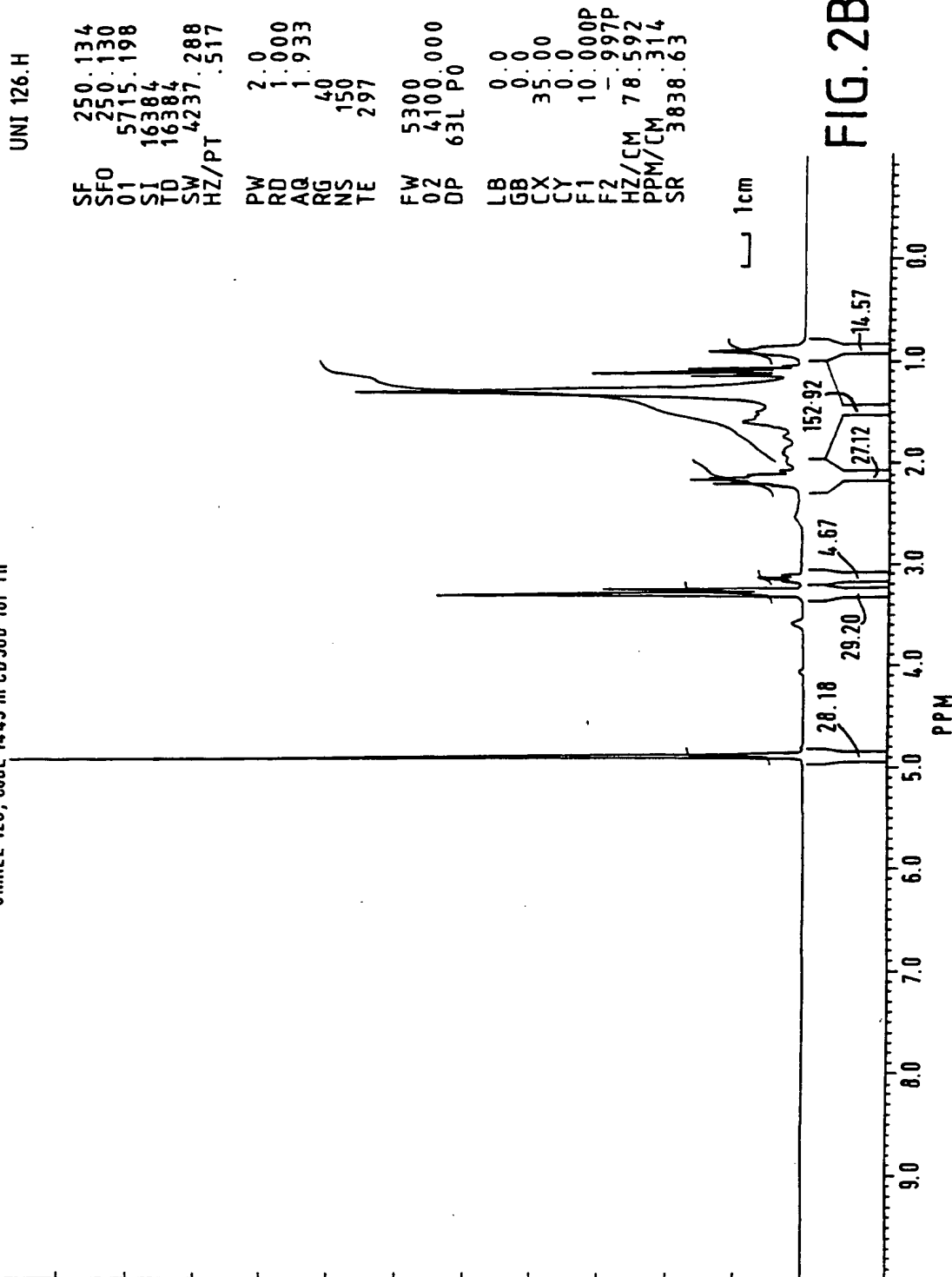


FIG. 2B2.

FIG. 2B3.



UNIREZ 126, CODE 1449 in CD 30D for 1H





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GLASS TRANSITION	
AUTOLIMIT	0/1
START TEMP. °C	10
END TEMP. °C	200
BASELINE TYPE	1
PLOT CM	10
PLOT MODE	101
IDENT. NO.	142
RATE K/MIN.	5
WEIGHT mg	11.10
END SCREEN °C	198.2

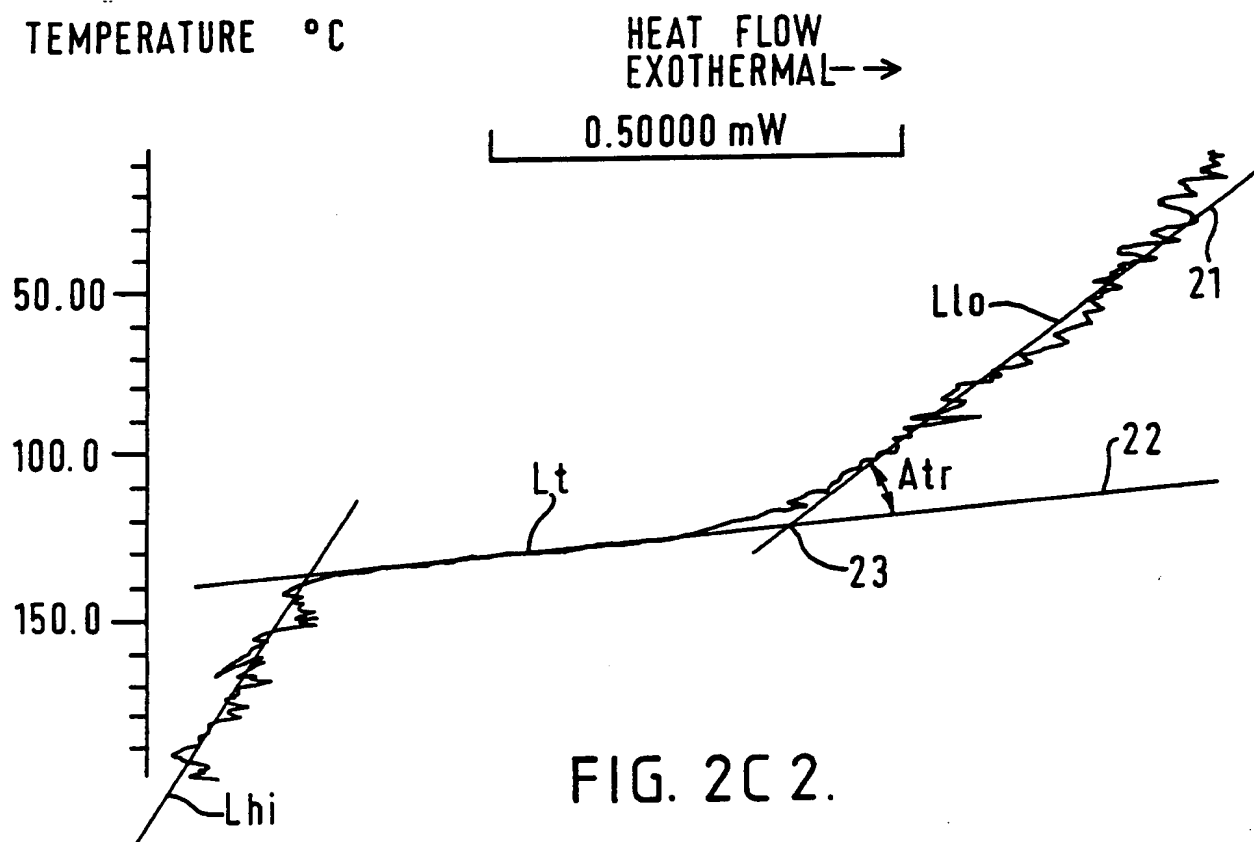


FIG. 2C 2.

FIG. 2C3.

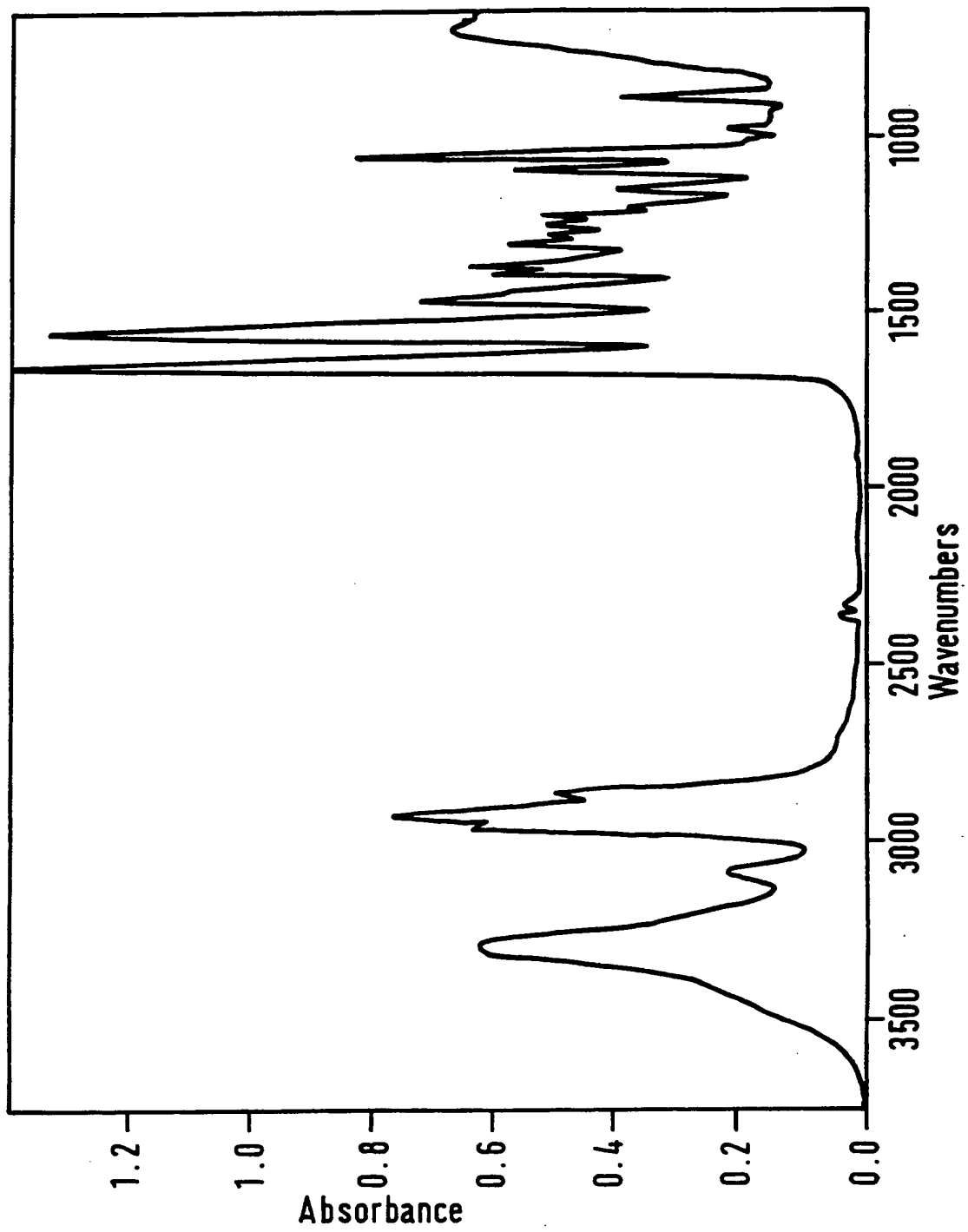
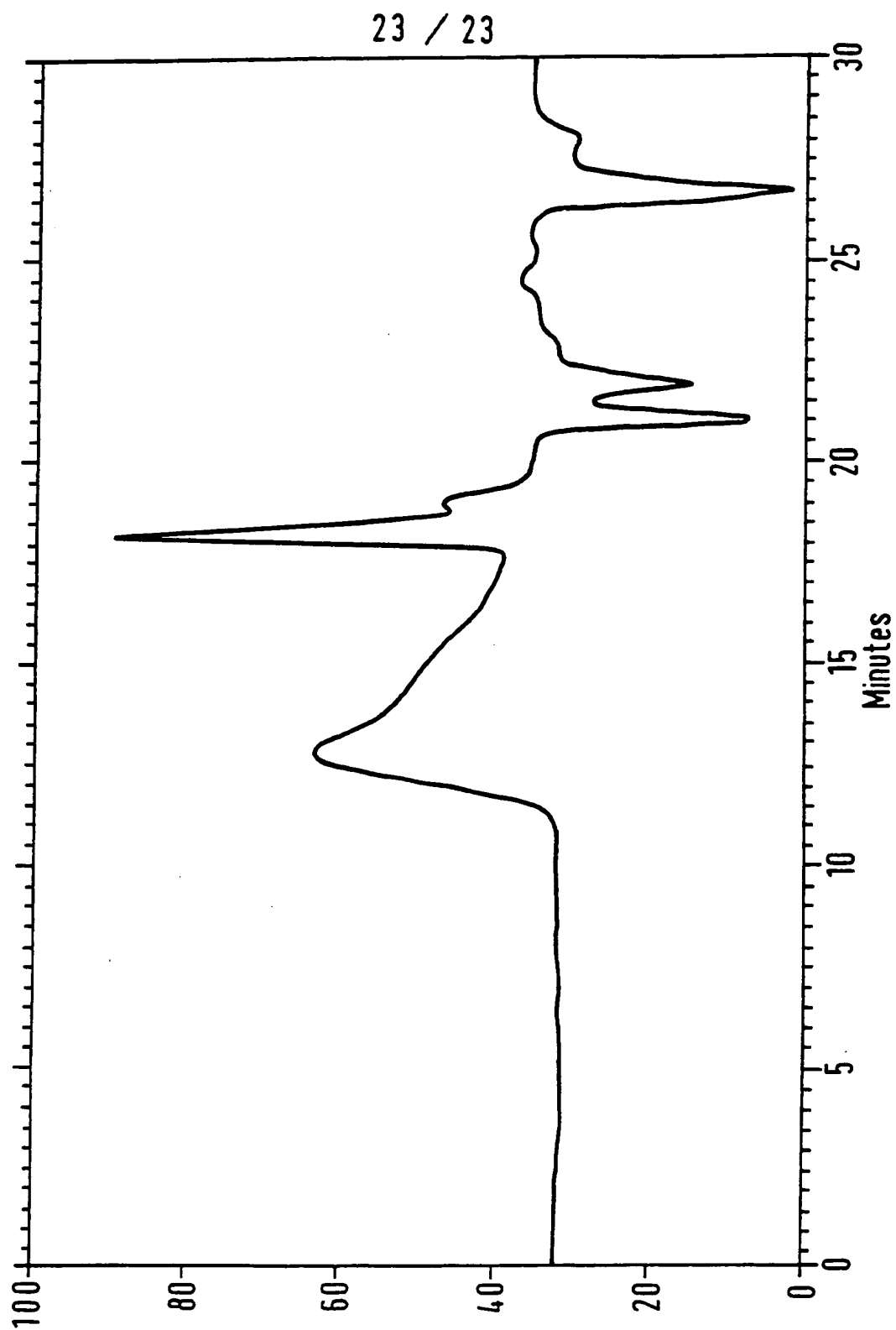


FIG. 2C5.



INKS

The present invention relates to inks for ink jet printers and especially those which operate continuously.

5 It will be described with reference to such printers but it will be appreciated that the inks described herein may also find uses in a far wider range of less demanding applications, such as drop on demand.

10 An ink jet printer projects from a printer head a stream of ink droplets to impact on the substrate to be marked as the substrate is conveyed, typically at high speed, past the head. The droplets are controlled, typically electrically, so that they are deposited in a controlled array and the substrate is thereby printed  
15 with a desired indicia. Typically such indicia are code numbers and letters, dates such as "sell by" dates and other alphanumeric data, such as mail addressing. Precision is clearly essential as well as high speed.

20 In addition whilst the jet will be continuously operating during a printing run, the ink must also be stable physically and chemically during periods between runs.

Ink which is not deposited on the substrate is collected automatically and recycled to a return tank.  
25 To enable the ink to be applied in this way it has to have a viscosity held to close limits. In addition in order for the ink to dry or set on the substrate it is necessary for components of the ink to evaporate off from the image on the substrate. Accordingly to maintain  
30 sufficient fluidity a make up fluid has to be added to the return tank to replace lost fluids.

Typically an ink jet ink contains a colouring agent, a liquid vehicle, and a polymer. The adhesion of the polymer to the substrate and thus the adhesion of the

image may be increased by adhesion promoters, such as agents effective to cross link the polymer, to form bonds between the polymer and the substrate or to do both.

5 In addition, where droplet formation and control is achieved electrically, it is necessary for the ink to be electrically conductive. Conductivity may be imparted by the colouring agent when this includes a charged species. If it does not impart sufficient or any conductivity this may be provided by a conductivity controller, e.g. a species ionizable in the ink, e.g. in the liquid vehicle, 10 such as an inorganic salt or an organic salt.

The art is constantly striving to achieve deposits of sufficient durability on an increasing range of substrates. Some have concerned themselves with printing 15 on glass or glazed ceramics (e.g. GB 1451937 and 1524881). Others have concerned themselves with polymer substrates such as acrylonitrile butadiene styrene polymers (ABS); polyolefins, such as polyethylene; polystyrene; polyvinyl chloride (PVC), plasticized or 20 unplasticized; polyesters; and cellulose. Metal surfaces such as aluminium and stainless steel are also important substrates as are papers.

With regard to the colouring agent this has usually been related to the liquid vehicle. The colouring agents 25 may be soluble in organic solvents e.g. methyl ethyl ketone, or  $C_{1-5}$  alcohols e.g. methanol or ethanol (for example as industrial methylated spirits) or they may be soluble in alcohols mixed with water, or soluble in both alcohol and water.

30 Examples of colouring agents which have been advocated for use in ink jet inks are dyestuffs soluble in alcohol alone such as Basic Blue 81, Solvent Orange 7 and Solvent Blue 58. Examples which are soluble in alcohol and water are Basic Violet 10, Acid Red 52, Acid

Black 1, Acid Blue 59, Acid Red 73 and Acid Blue 9.

Triarylmethane dyes have also been advocated. Examples of these are Crystal Violet F<sub>n</sub> (available from BASF) and Victoria Blue B base (available from Hilton Davis).

The colouring agents are employed in amounts appropriate to give the desired colour intensity in the deposit. Typically the ink contains 0.1 to 10% of the colouring agent e.g. 3 to 7% preferably 4 to 6%.

The liquid vehicle has to be such as to impart the desired fluidity (or low viscosity) to the ink but must evaporate at a high enough rate to leave the deposited image resistant to smudging soon after it is deposited. It must also be a good enough solvent to get the colouring agent and polymer intimately admixed.

Methyl ethyl ketone (MEK) has been used very effectively in commercially available ink jet formulations, as has ethyl acetate. However, these are thought to have adverse effects on the environment. It is thus desired to replace them with other liquid vehicles. Alcohols and mixtures of alcohols and water have been advocated (see GB 1541937 and 1524881).

However MEK systems give good adhesion to many substrates and evaporates rapidly giving a short smudge time - typically the deposit becomes dry and smudge free within 2 seconds.

The polymer has the function of carrying the colouring agent and adhering it to the substrate. A number of polymers have been advocated.

Acid catalysed phenol aldehyde condensation polymers of molecular weights in the range 200-2500 which are linear and relatively free of cross linking, alcohol soluble and tolerant of dilution in the water have been proposed in GB 1541937 and 1524881. Their common name is

novolac resins. Polyester resins, acrylic resins e.g. styrene - (alkyl) acrylic acid copolymer resins (see GB 2053948) and polyketone resins have also been used or proposed.

5           Adhesion promoters have been mentioned above and one class of these materials are cross linking agents, which can be used to advantage to improve adhesion to certain substrates.

10           A preferred cross linking agent is one which has functional groups which can react with functional groups such as hydroxyl in the polymer which have labile acidic protons. In the presence of water or alcohol it is believed that the reactivity of these reactive groups in the polymer will be suppressed but as the water and  
15           alcohol evaporate from the deposited image it is believed that such a cross linking agent can react with these groups in the polymer and possibly in the substrate. Whether this is the true mechanism or not the effect seems to be to increase the adhesion of the deposit to  
20           the substrate.

          Examples of preferred cross linking agents which are believed to operate in the above described way are transition metals coordinated with OR or acid groups. For example, the agent may have the formula  $(RO)_m Mx_n$  wherein  
25           M is the metal, R is an alkyl group, X is a phosphate residue, and m and n are each integers (or one, e.g. n may be zero) whose total is the oxidation state of M. M is preferably titanium.

30           An example of such a compound is titanium tributyl phosphate.

          GB 2161811 (Tioxide) describes the production of such compounds and refers to their use as adhesion promoters in inks, mentioning photogravure and flexographic inks specifically.

invention.

5       The line Lt makes an acute angle (Atr) with the line Llo. When Atr is less than  $10^\circ$  the transition is called weak. We prefer Atr to be at least  $20^\circ$ ,  $25^\circ$ ,  $30^\circ$ ,  $35^\circ$ ,  $40^\circ$ , or more preferably at least  $30^\circ$ . We prefer the transition to be not a weak transition.

10       If the  $T_{g0}$  is less than  $95^\circ\text{C}$  the drying time tends to be unacceptably long especially when the liquid vehicle is a  $\text{C}_{1-5}$  alcohol e.g. ethanol or industrial methylated spirits (IMS), of which there are various grades typically containing at least 95% by weight of ethanol and balance of methanol and other denaturants.

15       When the  $T_{g0}$  is greater than  $175^\circ\text{C}$  it may be expected that a decrease in solubility will occur making the ink unsuitable for ink jet purposes.

20       We have found that excellent results are obtained when the polymer is an alcohol soluble polyamide. Alcohol solubility is enhanced when the polyamide is made up of aliphatic groups and preferably these predominate in the molecule, which may indeed be fully aliphatic.

25       The polyamide is preferably one of which the IR spectrum exhibits an absorption peak at a wavenumber in the range of 2920 to 2930 which is characteristic of the presence of alkyl groups and an absorption peak at a wavenumber in the range of 1635 to 1645 which is characteristic of the amide I group and desirably does not exhibit absorption peaks characteristic of an aromatic group.

30       The ratio of the absorbance of the alkyl peaks to that of the amide peaks is preferably not greater than 0.7:1, or 0.6:1 and is preferably in the range 0.55:1 to 0.01:1 or more preferably 0.55:1 to 0.1:1 or 0.55:1 to 0.2:1 or 0.3:1 or 0.4:1.



The liquid vehicle is preferably a C<sub>1-5</sub> alcohol e.g. methanol or ethanol and especially IMS.

5 Preferably the polyamide is one which is soluble in ethanol at 25°C at least to the extent that a solution of 10% by weight of polyamide based on solvent and polyamide can exist at 25°C.

10 The colouring agent is preferably a dyestuff soluble in the liquid vehicle, preferably an alcohol soluble one, especially one soluble in IMS; however very finely divided pigments could be contemplated.

Preferred colouring agents are chrome based complex dyes such as chrome azo dyes for example Solvent Black 29. A preferred form of such chrome azo dye is Solvent Black 29 having an infra-red spectra having no significant peak in the range 1650 to 1750.

15 The amount of polymer based on the ink by weight is preferably in the range 2% to 20% e.g. 5% to 15% especially 7% to 12%.

20 The amount of colouring agent based on the ink by weight is preferably in the range 0.1 % to 15% e.g. 0.5% to 10% especially 4% to 7%.

25 The amount of liquid vehicle is typically the balance of the composition and is typically, based on the ink by weight, in the range 65% to 95%, preferably 75 to 95%.

30 As mentioned above the composition may also contain an adhesion promoter. This may be a cross linking agent effective to cross link the binder polymer at least in the deposit. Desirably the polymer is chosen to be cross linkable in this way.

Preferred cross linking agents are the metal phosphate chelate type described above.

The cross linking agent may be present in an amount based on the ink by weight in the range 0.5% to 10% or

more importantly in an amount, based on the polymer binder by weight, in the range 1% to 40%, e.g. 10% to 35%, especially 20% to 30%.

5 As mentioned above the composition may also contain a conductivity controller e.g. an ionizable compound effective to make the ink of sufficient conductivity for ink jet printing.

Typically the conductivity controller may be present in an amount based on the ink by weight in the range 0.1% to 5% e.g. 0.5% to 3%, especially 0.75% to 2%.

10 The invention may be put into practice in various ways and a number of specific embodiments will be described to illustrate the invention with reference to the accompanying examples, in which all amounts are in % by weight unless otherwise stated.

15 In addition references will be made to the accompanying drawings in which:

Figure 1A1 is a differential scanning calorimetry (DSC) plot of the first run (the drying run) for the polyamide P4512 of Example 1A;

20 Figure 1A2 is a DSC plot of the second run (the measurement run) for the polyamide P4512 of Example 1A;

Figure 1A3 is an infra-red (IR) spectra for the polyamide P4512 of Example 1A;

25 Figure 1A4 is a nuclear magnetic resonance (NMR) spectra for the polyamide P4512 of Example 1A;

Figure 1A5 is a chromatogram (GPC) for the polyamide P4512 of Example 1A;

30 Figure 1A6 is an IR spectra of Valifast 3808 the dye used in Example 1.

Figure 1B1 is a DSC plot of the first run (the drying run) for the polyamide Eurelon 975 of Example 1B;

Figure 1B2 is a DSC plot of the second run (the

measurement run) for the polyamide Eurelon 975 of Example 1B;

Figure 1B3 is an IR spectra for the polyamide Eurelon 975 of Example 1B;

5        Figure 1B4 is an NMR spectra for the polyamide Eurelon 975 of Example 1B

Figure 1B5 is a chromatogram produced on gel permeation chromatography (GPC) apparatus for the polyamide Eurelon 975 of Example 1B;

10       Figure 2A2 is a DSC plot of the second run (the measurement run) for the polyamide Eurelon 966 of Example 2B;

Figure 2A3 is an IR spectra for the polyamide Eurelon 966 of Example 2B;

15       Figure 2A4 is an NMR spectra for the polyamide Eurelon 966 of Example 2B;

Figure 2A5 is a chromatogram (GPC) for the polyamide Eurelon 966 of Example 2B;

20       Figure 2B2 is a DSC plot of the second run (the measurement run) for the polyamide UNIREZ 126 of Example 2C;

Figure 2B3 is an IR spectra for the polyamide UNIREZ 126 of Example 2C;

25       Figure 2B4 is an NMR spectra for the polyamide UNIREZ 126 of Example 2C;

Figure 2B5 is a chromatogram (GPC) for the polyamide UNIREZ 126 of example 2C;

30       Figure 2C2 is a DSC plot of the second run (the measurement run) for the polyamide UNIREZ 150 of Example 2D;

Figure 2C3 is an IR spectra for the polyamide UNIREZ 150 of Example 2D;

Figure 2C4 is an NMR spectra for the polyamide UNIREZ 150 of Example 2D:

Figure 2C5 is a chromatogram (GPC) for the polyamide UNIREZ 150 of Example 2D;

Example 1

5

Inks were formulated as given in Table 1 below, which also gives certain physical properties of the inks.

Table I

10	Example	1A	1B
	Ingredient		
	<u>Colouring agent</u>		
	chromium azo dye (1)	4.3	5.5
15	<u>Liquid vehicle</u>		
	IMS	79.0	79.5
	<u>Polymer binder</u>		
	polyamide (2)	12.7	-
	polyamide (3)	-	10.0
20	T <sub>g</sub> O	-	125°C
	T <sub>g</sub> R	-	15°C
	Atr	-	45°
	Cross linking agent		
	titanium phosphate chelate (4)	3.2	4.0
25	<u>Conductivity controller</u>		
	lithium nitrate	0.8	1.0
	<u>Properties</u>		
	viscosity (5)	6.5	6.4
	in mPa*s (centipoise)		
30	conductivity (6)	>700	>700
	μS/cm		
	surface tension at 25°C (7)	24-27	24-27
	dynes/cm		
	density (8) g/cm <sup>3</sup>	0.8-0.9	0.8-0.9

Notes on Table 1

5 (1) This chromium azo dye is supplied as Valifast 3808 by ICI from Orient Chemicals, USA. Its standard name is Solvent Black 29. It is soluble in IMS.

Figure 1A6 is an infra-red spectra of Valifast 3808. It will be observed that it does not exhibit a peak in the region 1600-1750.

10 (2) This polyamide is supplied as polyamide P4512 by Lawter International.

It has a melting point (Mercury) of 107-112°C.

It does not exhibit a Glass Transition.

15 DSC measurements were carried out using a METTLER DSC 30 system with a METTLER TA3000 processor using a rate of temperature rise of 5 °C per minute from -40 °C to 200 °C. DSC uses two pans which are heated and the heat input required to raise each pan by the same temperature is measured and the difference in heat input required is plotted against temperature. One pan was  
20 used as the reference. The other pan contains the sample to be tested. The procedure is to do a first run to drive off solvents and other volatiles, after which the sample is allowed to cool. The heating cycle is then repeated immediately.

25 Figure 1A1 is the plot of the first run and Figure 1A2 is the plot of the second run for polyamide P4512. If a Glass Transition was occurring it would be seen from Figure 1A2 that the plot would follow a straight base line as the temperature is increased from low values. A  
30 best straight line would be drawn for this region from 0°C to the step change to give a base line 21. The plot would then go through a step change in the heat flow which would manifest itself in the plot as an inflexion. A best tangent to the inflexion would be drawn to give a

line 22. The lines 21 and 22 would be extended until they intersected at the point 23. The point of intersection would be the  $T_g$  onset value herein.

5 Polyamide P4512 has the following physical characteristics:

(i) an infrared (IR) spectra as shown in Figure 1A3, with the following significant peaks-

2925 wavenumber denoting the presence of alkyl groups, 1640 wavenumber, the amide 1 band, denoting the presence  
10 of amide groups. The ratio of absorbance of the alkyl peak or band to the amide peak is 1:1.

The IR spectra was carried out using attenuated total reflectance, zinc selenide crystal and an incident-angle of 45°C.

15 (ii) a nuclear magnetic resonance (NMR) spectra as shown in Figure 1A4, with the following significant peaks-

4.9-5.0 ppm denoting the presence of amide groups, 0.8-1.8 ppm denoting the presence of alkyl groups, the peak  
20 at 1.3 ppm being characteristic of methylene and the peak at 0.9 being characteristic of methyl. Substantial peaks at 3.3 ppm and at 2.2 ppm are also present.

The NMR spectra was carried out with the system locked onto tetramethyl silane as the reference material.  
25  $^1\text{H}$  nmr spectra were recorded on a Bruker AC250 spectrometer (250 MHz) after dissolving the sample in  $\text{CD}_3\text{OD}$ .

The polymer can be deduced to contain solely aliphatic components, see the IR and NMR spectra.

30 (iii) a chromatogram (GPC) as shown in Figure 1A5.

This was carried out as described below for Figure 1B5.

(3) This polyamide is supplied as polyamide Eurelon 975 by Witco.

It has a softening point as determined by the ball and ring method of 173°C.

5 It exhibits a Glass Transition and has a  $T_g$  onset value of 125 °C, a  $T_gR$  range of 125 °C to 140 °C and an angle  $A_{tr}$  of 45°. These properties were measured by DSC using the method described above for the P4512 polyamide.

10 Figure 1B1 is the plot of the first run and Figure 1B2 is the plot of the second run for polyamide Eurelon 975. It will be seen from Figure 1B2 that a Glass Transition has occurred. Thus the plot follows a straight base line as the temperature is increased from low values. A best straight line is drawn for this region from 0°C to the step change to give a base line 21. The plot then goes through a step change in the heat flow which manifests itself in the plot as an inflexion. A best tangent to the inflexion is drawn to give a line 22. The lines 21 and 22 are extended until they intersect at the point 23. The point of intersection is the  $T_g$  onset value herein.

20 Polyamide Eurelon 975 has the following physical characteristics:

(i) an infrared (IR) spectra as shown in Figure 1B3, with the following significant peaks-  
25 2925 denoting the presence of alkyl groups, 1640, the amide 1 band, denoting the presence of amide groups.

The ratio of the absorbance of the alkyl peak or band to the amide peak is 0.54:1.

The IR spectra was carried out as above.

30 (ii) a nuclear magnetic resonance (NMR) spectra as shown in Figure 1B4, with the following significant peaks-

4.9 ppm denoting the presence of amide groups, 0.9 to 1.7 denoting the presence of alkyl groups, the methylene peak at 1.3 ppm and the methyl peak at 0.9 being present, but

only small peaks being present in the range 2 to 4 ppm.

The NMR spectra was carried out as above.

(iii) a GPC chromatogram as shown in Figure 1B5.

5 The horizontal axis is in minutes, the vertical axis is in % detector response.

The chromatogram shown in Figure 1B5 was produced on a gel permeation chromatography column using isopropanol as the eluant. Two columns were used in series. The first was composed of PL gel 5 micrometres and had a porosity of  $10^3$  Angstroms, the second was composed of PL gel 5 micrometres and had a porosity of 50 Angstroms.

10 The detector was a Waters 410 refractive index detector and gives an output in millivolts. This is plotted as % detector response against time in minutes since the sample was injected. The flow rate of the solvent through the column was 1.00 ml/min. The samples were prepared by dissolving in isopropanol to give a concentration of 0.25% by weight of the polymer. The samples were injected as 100 microlitre samples.

20 The chromatogram shows a peak at 10 to 12 minutes with a sharp lower time face and a shallow higher time face. It is suspected that this may be due to the polymer becoming absorbed onto the column in a way more characteristic of liquid chromatography than of gel permeation chromatography. However whatever the cause the effect is repeatable and appears to be characteristic of the polymer.

25 The chromatogram also has a sharp peak at about 17 minutes and then a more complicated pattern at higher times.

30 The polymer can be deduced to contain solely aliphatic components, see the IR and NMR spectra.

(4) This titanium phosphate chelate is supplied as



Tilcom IA10 (Registered Trade Mark) by Tioxide Chemicals, Cleveland, U.K. as a 65% by weight solution in isopropanol.

5 (5) Viscosity is measured using a Brookfield Viscometer (model DV-II) with an ultra low (UL) adaptor, set to 60 r.p.m. All measurements are carried out in a thermostatically controlled water bath at 25° and ink samples are equilibrated at this temperature prior to  
10 measurement.

(6) Conductivity is measured directly using an EDT series conductivity meter (model 3 BA380) which is solvent resistant. The conductivity probe is a platinum  
15 plate ( $1\text{cm} \approx 1\text{m}^{-1}$ ).

All measurements were carried out after calibration of the meter and equilibration of the ink in a water bath held at 25°C.

20 (7) Surface tension is measured using a torsion balance with a platinum ring at 25°C.

(8) Density is measured using a pyknometer (density  
25 bottle) at 25°C.

The inks of Example 1A and 1B were compared by applying them using the same ink jet printer with means for heating the printer head so that the droplets are held at a fixed temperature when projected onto an  
30 aluminium substrate, a polycarbonate substrate and an enamel coated steel substrate. The head was held at 25 °C. The two examples were compared with a conventional ink in which the liquid vehicle was MEK and the polymer binder was a nitrocellulose which is insoluble in IMS.

This conventional ink is referred to as Example 1C.

The time for the deposit to become non smudging (the drying time) is given in Table II.

Table II

5	<u>Substrate</u>	<u>Aluminium poly-</u>	<u>Enamel</u>	<u>Ad-</u>
			<u>coated</u>	<u>hesion</u>
	Example	<u>carbonate</u>	<u>steel</u>	(10)
	1A	1.0	3.5 (9)	4.0 (9)
	1B	1.25	1.75	1.5
10	1C	1	1	1
	Note on Table II			

(9) These deposits remained tacky for longer than the recorded drying time.

15 (10) Adhesion was assessed by determining the scrub resistance under wet conditions of printed codes. Solid blocks were printed on the substrate, the blocks consisting of a 16 x 10 dot matrix 5 mm high at a density of 10 blocks in a 6 cm line. The substrate was mounted on a Sheen abrasion tester (model 903A) and abraded with the nylon brush supplied with the machine whilst wet with water. The test is considered to be failed when an area equivalent to a single block has been removed from the substrate. The test is normally carried out for up to 20 700 oscillations of the brush. If failure occurs before 200 cycles adhesion is poor, failure between 201 and 600 is described as good, and if no failure has occurred at 25 600 cycles then adhesion is excellent.

30 The ink of Example 1B containing the polymer with the higher  $T_g$  value gives a considerably improved drying time compared to Example 1A.

The time for the deposit to become non smudging was assessed as follows:

The image projected onto the substrate was of

alphanumeric characters, the alphabet and the numbers 1-9, 3mm high with 7 characters to the inch (2.75/cm). Each character falls within a 7x5 dot matrix and the characters are arranged in a single print line. The substrate is located 13mm from the print head and moved past the print head at 1 metre per second. The print head has a 75 micrometre (micron) diameter nozzle. A finger is drawn across the image repeatedly at about 0.25 second intervals until the image no longer smudged. The time to the first non-smudged image was judged to be the drying time to the nearest 0.25 second.

These tests were then repeated for examples 1A and 1B using the same ink jet printer.

The head was heated to 50 +/- 3°C and the results are given in Table III.

Table III

<u>Substrate</u>	<u>Aluminium</u>	<u>poly-carbonate</u>	<u>Enamel coated steel</u>
Example			
1A	1.0	3.5	4.25
1B	1.0	1.5	1.5

Example 1B with the higher  $T_g$  onset value has much improved performance on polycarbonate and enamel coated steel compared to Example 1A. The drying times for Example 1B are competitive with those for 1C whilst those of Example 1A are not.

Examples 2A, 2B, 2C, 2D

Inks were formulated as given in Table IV below which also gives certain physical properties of the inks.

These examples demonstrate the effect of varying the onset  $T_g$  value on drying time and wear properties.

Table IV

	<u>Example</u>	<u>2A</u>	<u>2B</u>	<u>2C</u>	<u>2D</u>	<u>2E</u>
	<u>Ingredient</u>					
5	<u>Colouring agent</u>					
	Dye (1)	5.5	5.5	5.5	5.5	5.5
	<u>Liquid vehicle</u>					
	IMS 99	83.8	83.5	83.5	83.5	83.5
	(96% ethanol)					
10	<u>Polymer binder</u>					
	polyamide (3)	10.0				
	polyamide (11)		10.0			
	polyamide (12)			10.0		
	polyamide (13)				10.0	
15	polyamide (2)					10.0
	T <sub>g</sub> o	125°C	-	-	130°C	-
	T <sub>g</sub> R	15°C	-	-	10°C	-
	Atr	45°C	-	-	34°C	-
	<u>Cross linking agent</u>					
20		-	-			-
	<u>Conductivity controller</u>					
	lithium nitrate	1.0	1.0	1.0	1.0	1.0
	<u>Properties</u>					
	viscosity (5)	6.2	2.8	2.9	6.1	3.6
25	conductivity (6)	1299	1757	1842	1387	1383
	surface tension (7)	24.5	24.5	25.3	24.5	25.1
	density (8)	0.8	0.8	0.8	0.8	0.8
		0.9	0.9	0.9	0.9	0.9

Notes on Table IV

Notes (1), (3) and (5) to (8) are as given for Table I

35 (11) This polyamide is supplied as polyamide Euralon 966

by Witco. It has a softening point as determined by the ball and ring method of 118°C. It does not exhibit a Glass Transition. An attempt to determine Glass Transition was made by DSC using the method described under note (3) above.

Figure 2A2 is the plot of the second DSC run for polyamide (11).

Polyamide Eurelon 966 has the following physical characteristics:

(i) an infrared (IR) spectra as shown in Figure 2A3, with the following significant peaks- 2925 denoting the presence of alkyl groups, 1640, the amide 1 band, denoting the presence of amide groups.

The ratio of absorbance of the alkyl peak or band to the amide peak is 1:1.

The IR spectra was carried out as above.

(ii) a nuclear magnetic resonance (NMR) spectra as shown in Figure 2A4, with the following significant peaks-

4.9 ppm denoting the presence of amide groups, 0.9 to 2.7 denoting the presence of alkyl groups, the methylene peak at 1.3 ppm and the methyl peak at 0.9 being present. Substantial peaks at 3.3 and 1.9 ppm are also present.

The NMR spectra was carried out as described above for Figure 1A4.

(iii) a chromatogram (GPC) as shown in Figure 2A5. This was produced using the same conditions as described above for Figure 1B5.

The chromatogram does not show a peak at less than 15 minutes.

The polymer can be deduced to contain solely aliphatic components, see the IR and NMR spectra

(12) This polyamide is supplied as polyamide UNIREZ 126 by Union Camp. It has a softening point as determined by

the ball and ring method of 115°C. According to the manufacturer this polymer has a molecular weight in the range 1600-1700.

5 It does not exhibit a Glass Transition. An attempt to determine Glass Transition was made by DSC using the method described under note (3) above.

Figure 2B2 is the plot of the second DSC run for polyamide (12).

10 Polyamide UNIREZ 126 has the following physical characteristics:

(i) an infrared (IR) spectra as shown in Figure 2B3, with the following significant peaks-

2925 denoting the presence of alkyl groups, 1640, the amide 1 band, denoting the presence of amide groups.

15 The ratio of absorbance of the alkyl peak or band to the amide peak is 0.82:1.

The IR spectra was carried out as above.

20 (ii) a nuclear magnetic resonance (NMR) spectra as shown in Figure 2B4, with the following significant peaks-

4.9 ppm denoting the presence of amide groups, 0.9 to 1.6 ppm denoting the presence of alkyl groups, the methylene 1.3 ppm and methyl 0.9 ppm peaks being present. A substantial peak at 3.3 ppm is also present.

25 The NMR spectra was carried out as described above for Figure 1A4.

(iii) a chromatogram (GPC) as shown in Figure 2B5. This was produced using the same conditions as described above for Figure 1B5.

30 The chromatogram does not show a peak at less than 15 minutes.

The polymer can be deduced to contain solely aliphatic components, see the IR and NMR

(13) This polyamide is supplied as polyamide UNIREZ 150

by Union Camp. It has a softening point as determined by the ball and ring method of 165°C. According to the manufacturer this polymer has a molecular weight in the range 1600-1700.

5           It exhibits a Glass Transition and has a  $T_g$  onset value of 130°C, a  $T_gR$  range of 130°C to 140°C and an angle  $A_{tr}$  of 34°C. These properties were measured by DSC using the method described under note (3) above.

10           Figure 2C2 is the plot of the second DSC run for polyamide (13). It will be seen from Figure 2C2 that the plot follows a straight base line as the temperature is increased from low values. A best straight line is drawn for this region to give a base line 21. The plot then goes through a step change in the heat flow which  
15           manifests itself in the plot as an inflexion. A best tangent to the inflexion is drawn to give a line 22. The lines 21 and 22 are extended until they intersect at the point 23. The point of intersection is the  $T_g$  onset value herein.

20           Polyamide UNIREZ 150 has the following physical characteristics:

          (i) an infrared (IR) spectra as shown in Figure 2C3, with the following significant peaks-  
2925 denoting the presence of alkyl groups, 1640, the  
25           amide 1 bond, denoting the presence of amide groups.

          The ratio of absorbance of the alkyl peak or bond to the amide peak is 0.54:1.

          The IR spectra was carried out as above

30           (ii) a nuclear magnetic resonance (NMR) spectra as shown in Figure 2C4, with the following significant peaks-

4.9 ppm denoting the presence of amide groups, 0.9 to 1.7 ppm denoting the presence of alkyl groups, the methylene peak at 1.3 ppm and methyl peak at 0.9 ppm being present

but only small peaks being present in the range 2 to 4 ppm.

The NMR spectra was carried out as described above for Figure 1A4.

5 (iii) a chromatogram (GPC) as shown in Figure 2C5. This was produced using the same conditions as described above for Figure 1B5. The chromatogram shows a peak at 10-12 minutes similar in shape but not as high as that shown in Figure 1B5. As for that polymer this effect is  
10 repeatable. The pattern at higher times is similar to that in Figure 1B5.

The polymer can be deduced to contain solely aliphatic components, see the IR and NMR and spectra.

15 The inks of Example 2A to 2E were compared by applying them using the same ink jet printer as for Examples 1A and 1B. The head was held at 25 °C.

The time for the deposit to become non smudging (the drying time) is given in Table V.

Table V

20

<u>Substrate</u>	Enamel coated Steel	Adhesion (10) (14)
Example		
2A	2	excellent
2B	4	excellent
25 2C	5	excellent
2D	2	excellent
2E	4	excellent

Note on Table V

30

(14) Adhesion was measured on orientated polypropylene film.



CLAIMS

1. An ink comprising a colouring agent, a liquid vehicle and a binder polymer characterised in that the polymer exhibits a Glass Transition.
2. An ink as claimed in claim 1 characterised in that the polymer has a Glass Transition Onset temperature in excess of 95°C.
3. An ink as claimed in claim 1 or 2 characterised in that it has a Glass Transition Onset temperature in the range 95°C to 175°C.
4. An ink as claimed in claim 1, 2 or 3 characterised in that the binder is a polyamide which exhibits a Glass Transition.
5. An ink as claimed in claim 1, 2, 3 or 4 characterised in that the binder is soluble in ethanol or IMS.
6. An ink as claimed in anyone of claims 1 to 5 characterised in that the binder exhibits IR absorption bands which denote the presence of alkyl groups including absorption at a wavenumber in the range of 2920 to 2930 and amide groups such as absorption at a wavenumber in the range of 1635 to 1645 but not aromatic groups which exhibit absorption at wavenumbers in the range of 3000 to 3200 and below 850.
7. An ink jet ink as claimed in anyone of claims 1 to 6 characterised in that the Glass Transition is not a weak transition.

8. An ink jet ink as claimed in anyone of claims 1 to 7 characterised in that the Glass Transition is such that the angle  $A_{tr}$  is at least  $30^{\circ}$ .

5 9. An ink jet ink as claimed in any one of claims 1 to 8 characterised in that the polymer is a polyamide which has an IR spectrum which exhibits an absorption peak at a wavenumber in the range of 2920 to 2930 which is characteristic of the presence of alkyl groups and an  
10 absorption peak at a wavenumber in the range of 1635 to 1645 which is characteristic of the amide 1 group and desirably does not exhibit absorption peaks characteristic of an aromatic group, and in that the  
15 ratio of the absorbance of the alkyl peaks to that of the amide peaks is not greater than 0.7:1.

20 10. An ink jet ink comprising a colouring agent, a liquid vehicle and a binder polymer characterised in that the polymer is a polyamide which has an IR spectrum which exhibits an absorption peak at a wavenumber in the range of 2920 to 2930 which is characteristic of the presence of alkyl groups and an absorption peak at a wavenumber in the range of 1635 to 1645 which is characteristic of the  
25 amide 1 group and desirably does not exhibit absorption peaks characteristic of an aromatic group, and in that the ratio of the absorbance of the alkyl peaks to that of the amide peaks is not greater than 0.7:1.

30 11. An ink jet ink as claimed in claim 9 or claim 10 characterised in that the ratio of the absorbance of the alkyl peaks to that of the amide peaks is in the range 0.7:1 to 0.01:1.

12. An ink jet ink as claimed in claim 9 or claim 10

characterised in that the ratio of the absorbance of the alkyl peaks to that of the amide peaks is in the range 0.6:1 to 0.1:1.

- 5      13. An ink jet ink as claimed in any one of claims 4 to 12 characterised in that the polyamide is one which is soluble in ethanol at 25°C at least to the extent that a solution of 10% by weight of polyamide based on solvent and polyamide can exist at 25°C.
- 10      14. An ink jet ink as claimed in any one of claims 1 to 13 characterised in that the colouring agent is a dyestuff soluble in alcohol or IMS.
- 15      15. An ink jet ink as claimed in claim 14 characterised in that the dyestuff is a chrome azo Solvent Black 29 dye having an infrared spectrum having no significant peak in the range 1650 to 1750 wavenumbers.

Search Examiner  
A J RUDGE

**Relevant Technical Fields**

- (i) UK Cl (Ed.M) C3V (VCA, VAE)  
(ii) Int Cl (Ed.5) C09D 11/10 C09D 11/10D

Date of completion of Search  
29 APRIL 1994

**Databases (see below)**

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-  
ALL

(ii) ONLINE DATABASE ED0C, CLAIMS, WPI, WPIL

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Category	Identity of document and relevant passages		Relevant to claim(s)
X,Y	GB 2238792 A	(COATES) eg Claim 5 and page 7 last paragraph	1-4 5-15
X,Y	EP 0359129 A2	(BASF) eg page 3 lines 15-21	1-4 5-15
Y	EP 0328301 A2	(UNION CAMP) see whole document	1-15
Y	US 4690712	(SUN) see claims	1-15
Y	US 4895888	(BASF) see whole document	1-15
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